Core-Functionalized Star Polymers by Transition Metal-Catalyzed Living Radical Polymerization. 1. Synthesis and Characterization of Star Polymers with PMMA Arms and Amide Cores[1]

Kyung-Youl Baek, Masami Kamigaito, and Mitsuo Sawamoto*

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-8501, Japan

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ABSTRACT: A series of microgel core-functionalized star-shaped polymers were synthesized by the polymer linking reaction method in $RuCl_2(PPh_3)_3$-catalyzed living radical polymerization. The synthesis was achieved by the polymer linking reaction method; i.e., functionalized divinyl compounds were added in situ to the solution of linear living poly(MMA)s prepared with the Ru(II)-catalyzed living radical polymerization. The functionalized microgel cores thus obtained contained acrylamide and methacrylamide. Also, star polymers with varying densities of the microgel cores were prepared from diacrylamides with various lengths and structures of the spacer, and by changing the relative amounts of MMA (arm length) and divinyl compound (core size) to initiator, a variety of core-functionalized star polymers could be obtained in high yield, These core-functionalized star-shaped polymers have f of 20−640, M_w of 3.3×10^5−1.3×10^7, and R_z of 5−42 nm. These results indicated that the cores carry as many as 440−51 000 amide groups in microgel networks.

Introduction

Multiarmed polymers have been attracting interest in various research fields, as their morphology, physical properties, and perhaps functions may considerably differ from those of the linear counterparts. Among them are star (-shaped) polymers where linear polymeric chains (arms) are radially attached onto a central moiety (core).[2] Living polymerization is one of the best methods to synthesize a variety of star polymers of well-defined architectures. It generally follows one of three methods: (a) living polymerization from a multifunctional initiator, (b) coupling reaction between linear living polymers and a multifunctional coupling (terminating) agents, and (c) linking reaction of linear living polymers with a divinyl compound (linking agents) via a soluble microgel core therefrom.[3]

Following the ample examples by living ionic predecessors, star polymers[4−20] can now be synthesized by radical living polymerizations,[21] and we have already shown that our Ru(II) complex-mediated living radical polymerization can be applied to the method (a)[6,7] and more recently to the method (c).[16] In particular, we are currently interested in the synthesis by the latter, the so-called "microgel" or "polymer-linking" approach,[22] because it provides us with a wide variety of star polymers carrying a relatively large number (from 10 to 1000) of arms per molecule, though the arm number here by definition involves a statistical distribution. Equally important, because the synthesis starts with a usual linear living propagation, it is rather straightforward to introduce functional groups into the pendant or the terminal groups of the arm chains.

Another unique feature of the microgel approach is that the core is usually a relatively large nanoscale microgel, derived from the linking agents, into which one may incorporate a large number of functional groups, a stimulus-responsive network, cavities for encapsulation, among others. Such designed and functionalized cores may not readily be obtained by other methods for star polymer syntheses. For example, these "core-functionalized" star polymers may be synthesized by using functional linking agents coupled with living radical polymerization, thanks to the general tolerance of radical processes toward polar functions (Scheme 1). However, few of them have been reported in either ionic or radical polymerizations.[23]

In this new series of papers, we will report the synthesis, characterization, and functions of "core-functionalized" star polymers obtained by the Ru(II)-mediated living radical polymerization.[24−28] This first paper discusses the feasibility of our synthetic approach for the core functionalization (Scheme 1), using a series of divinyl compounds in which the spacer, connecting two vinyl groups, carries polar functions such as amides, esters, and hydroxyl. Note that these functionalities need not be protected. Thus, methyl methacrylate (MMA) was polymerized with our typical Ru(II)-based initiating systems, and the resulting living polymers, without quenching and isolation, were allowed to react with functional linking agents (**1**−**7**). We herein report that this approach indeed leads to a series of "core-functionalized" MMA star polymers in high yield (except for **5**) and with varying size and core architectures. Discussion will be focused on the yield of the star polymers as a function of the spacer structure and reaction conditions, and the products are characterized in terms of absolute molecular weights, average number of arms per molecule, and radius of gyration.

Results and Discussion

Synthetic Feasibility of Core-Functionalized Star Polymers. To examine the synthetic feasibility of microgel core-functionalized star polymers by Ru(II)-catalyzed living radical polymerization (Scheme 1), we first utilized *N*,*N*′-methylenebis(acrylamide) (**1**) as a linking agent and analyzed the products obtained at each reaction step by size exclusion chromatography (SEC) as well as ^{1}H NMR and FT-IR spectroscopy.

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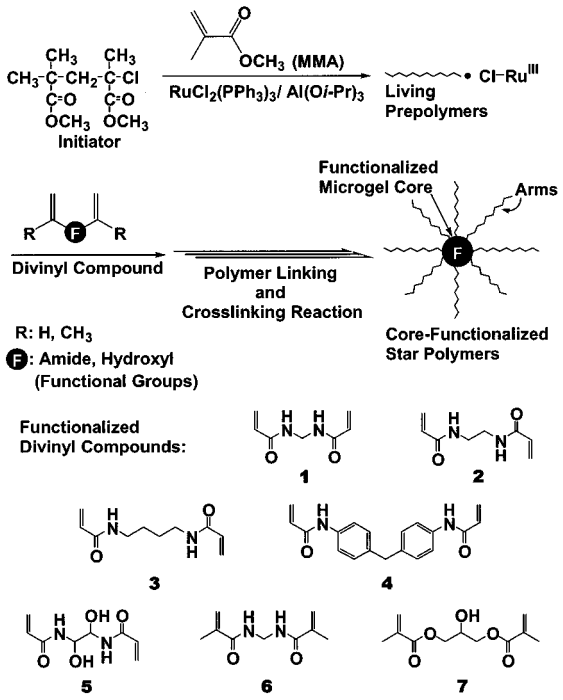
Scheme 1. Synthesis of Core-Functionalized Star-Shaped Polymers by Polymer Linking Reactions with Functionalized Divinyl Compounds



The first step was the now established living radical polymerization of methyl methacrylate (MMA) with $(MMA)_2$−Cl (initiator) coupled with $RuCl_2(PPh_3)_3$ (catalyst) and Al(O*i*-Pr)$_3$ (additive) in toluene at 80 °C.[27] The product was a linear poly(MMA) (P*) with a controlled molecular weight and a narrow molecular weight distribution (e.g., $M_n = 8.1 \times 10^3$; $M_w/M_n = 1.34$; conversion 88%; 94 h) (Figure 1A). To this living polymer solution (unquenched), a DMF solution of **1** (20 equiv to P*, $r = [\mathbf{1}]_0/[P^*]_0 = 20$) was added to induce a linking reaction. ^{1}H NMR analysis of the product obtained after 1 h showed that a block copolymer of MMA and **1** formed, where a short linear segment of **1** was attached to the starting PMMA, as observed as the olefin peaks (a) at 5.7−6.3 ppm (Figure 1F; also see Figure 1D for **1**). According to Scheme 1, the block copolymers are supposed to undergo, subsequently, inter- and intramolecular linking reactions between the living end and a pendant vinyl group, and this process turned out to be very fast for **1**. Thus, star polymers started to form simultaneously, while block copolymers were still forming (Figure 1B,C). As seen in Figure 1C, the major product in 5 h was the intended star polymers, with some block prepolymers remaining, and virtually no olefin pendant groups were detected by ^{1}H NMR (Figure 1G). These observations thus indicated the formation of the star polymer with a microgel core from **1**.

Because the near complete disappearance of the olefin peaks might be caused by the restricted mobility of the pendant groups in the dense microgel core, we further analyzed the products obtained at each step by FT-IR after fractionation by preparative SEC. Figure 2A−C shows the spectra of **1**, the linear living poly(MMA), and the product obtained after a 5 h linking reaction, which corresponded to the samples D, E, and G in Figure 1, respectively. Figure 2C shows not only the absorptions of the amide groups (3307 cm^{-1} for −NH−; 1672 cm^{-1} for −CO−) but also those of the ester groups (1731 cm^{-1}) derived from the poly(MMA) precursor. These results support that the final products were the core-functionalized star polymers with an acrylamide microgel core and poly(MMA) arm chains.

Design of Acrylamide Linking Agents. As we have shown for methacrylate-type linking agents,[16] design of the functionalized divinyl compounds is certainly important in the synthesis of the core-functionalized star polymers in high yield and with desired core functionality. For this, we compared acrylamide divinyl compounds (**1**−**4**) with varying spacers: as with **1**, compounds **2** and **3** have soft aliphatic spacers of different

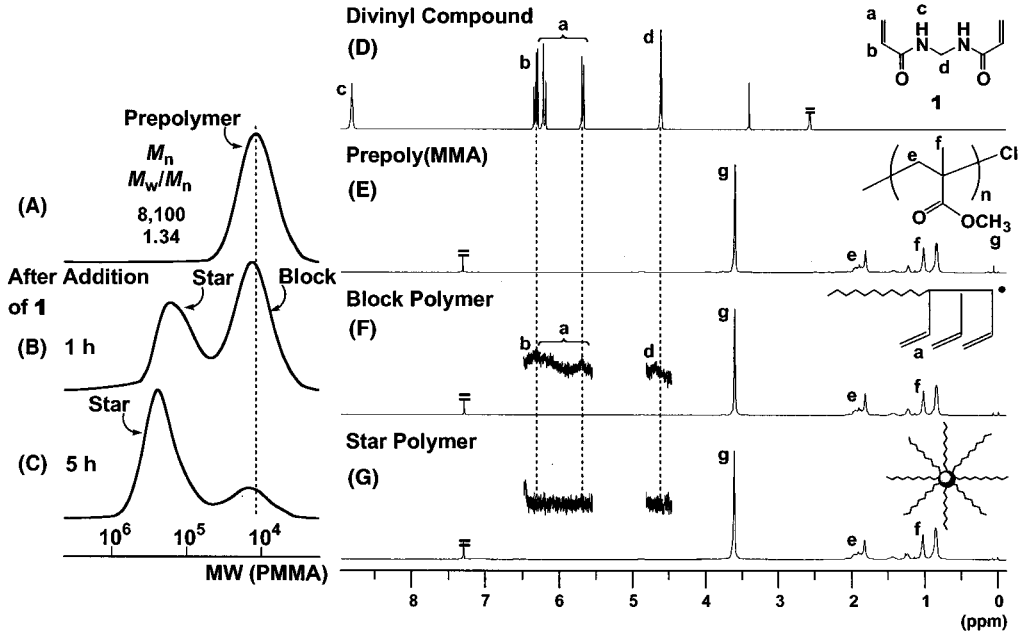


Figure 1. MWD and ^{1}H NMR spectra of the products obtained from the reaction of living poly(MMA) with divinyl compound **1** in toluene/DMF (5/3, v/v) at 80 °C: $[P^*]_0 = 20$ mM; DP (arm) = 100; $r = [\mathbf{1}]_0/[P^*]_0 = 20$. (A) Living poly(MMA): $[MMA]_0 = 2.0$ M; $[(MMA)_2\text{−Cl}]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[Al(Oi\text{-}Pr)_3]_0 = 40$ mM; MMA conversion = 88% in 94 h. (B, C) The products recovered after addition of **1** in 1 h (B) and 5 h (C). ^{1}H NMR spectra in $CDCl_3$ at room temperature: (D) divinyl compound **1**; (E−G) samples A−C, respectively.

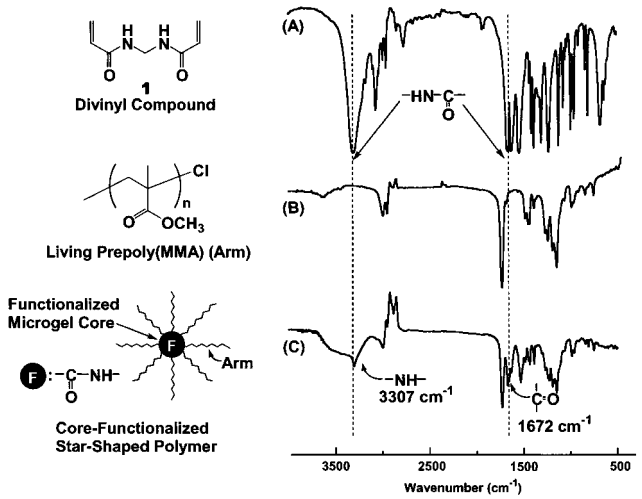


Figure 2. FT-IR spectra at room temperature: (A) divinyl compound **1**; (B) living poly(MMA); (C) the final product obtained at 5 h after addition of **1**. See Figure 1 for the reaction conditions.

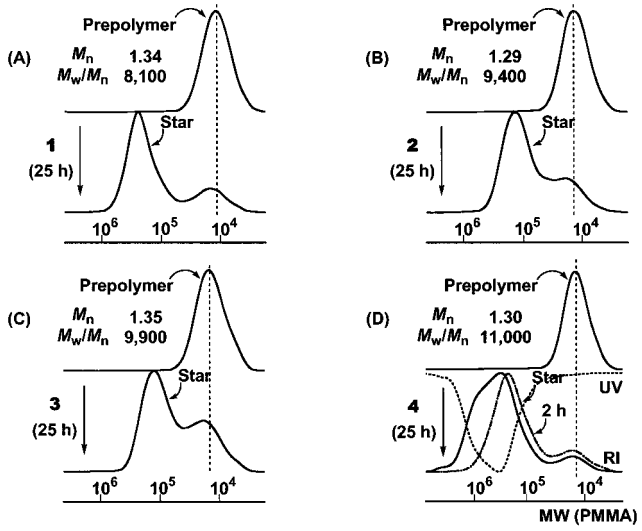


Figure 3. Core-functionalized star polymers obtained from living poly(MMA) with various acrylamide divinyl compounds (**1**−**4**) in toluene/DMF (5/3, v/v) at 80 °C: $[P^*]_0 = 20$ mM; DP (arm) = 100; $r = 10$.

lengths (**1** < **2** < **3**); **4** carries a rigid aromatic spacer. When applied to the living poly(MMA) in a toluene/DMF mixture (5/3 v/v) at 80 °C, the linking agents **2** and **3** gave star polymers in relatively high yields as **1** did (Figure 3A−C). The shorter the spacer in the linking agents, the higher the yield, i.e., **1** (78%) > **2** (74%) > **3** (68%). A longer aliphatic spacer might induce intramolecular cyclization and result in lower yield as observed with the methacrylate-type liking agents.[16]

Divinyl compound **4** led to star polymers in high yield in a relatively short time (2 h) (Figure 3D, dash−dotted line). However, they underwent further linking reaction (star−star coupling) to produce soluble products of higher molecular weights (Figure 3D; yield 90%). They exhibited intensive UV absorptions (Figure 3D, dashed line), which indicated that most of **4** was incorporated into the microgel core.

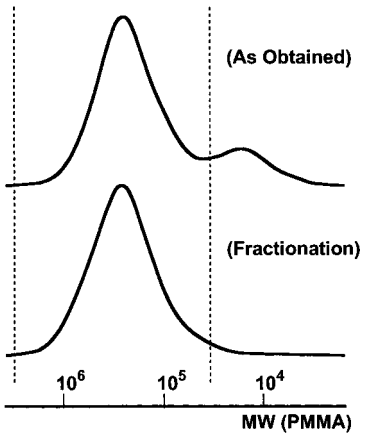


Figure 4. Fractionation of core-functionalized star polymers by SEC. The original sample from Figures 3D.

Polymer Characterization. The absolute molecular weights (M_w), the arm numbers (f), and the gyration radii (R_z) of the star polymers were characterized by multiangle laser light scattering (MALLS) coupled with SEC in DMF (Table 1). From samples obtained in similar yield (70−80%), higher molecular weight fractions (star polymers) were fractionated by preparative SEC. A typical example of fractionation is shown in Figure 4.

The obtained star polymers had M_w of 3.3×10^5−1.5×10^6 and R_z of 17−21 nm. The average number (f) of arms per star polymer was then calculated from M_w by MALLS/SEC and the M_w of the starting linear PMMA by SEC.[16] Thus, the star polymers from **1**−**4** have 22−82 arms/molecule. Especially, the star polymers from **4** (with a hard aromatic spacer) had obviously higher values of M_w, f, and R_z than those from **1**−**3** (with aliphatic segments).

The overall and apparent M_w determined by SEC was lower than those by MALLS, which is consistent with the expectation that the star polymers were more compact than the linear counterparts with the same molecular weights. This obvious conclusion was supported by the difference between the refractive index (RI) and the light scattering (LS) detectors traces of the star polymers in MALLS/SEC analysis (Figure 5), because the RI response only depends on the concentrations of molecules, whereas LS depend on the molecular weights as well as the concentrations of samples.

From these trends, **4** seems to be the most effective linking agent among the four, but the star polymers with **4** consist of aliphatic arm chains and an aromatic

Table 1. Star-Shaped Polymers with Various Acrylamide Microgel Cores[a]

divinyl compd	time[b] (h)	M_w (arm) (SEC)[c]	M_w/M_n (arm)	M_w (star) (SEC)	M_w (star) (MALLS)[d]	dn/dc[e] (mL/g)	f[f]	R_z[g] (nm)	yield[h] (%)
1	35	12 200	1.29	102 000	407 000	0.067	28	16.9	76
3	50	12 200	1.29	94 700	329 000	0.064	22		78
4	2	13 300	1.35	156 000	1 460 000	0.077	82	20.7	84

[a] Reaction conditions: $[P^*] = 20$ mM; DP (arm) = $[MMA]_0/[P^*]_0 = 100$; r (core) = $[\text{divinyl compound}]_0/[P^*]_0 = 10$ with $RuCl_2(PPh_3)_3$ and $Al(O\textit{i}\text{-}Pr)_3$ in the mixture of toluene and DMF (5/3 v/v) at 80 °C. [b] After addition of divinyl compound into the reaction solution of living poly(MMA). [c] Size-exclusion chromatography. [d] Multiangle laser light scattering. [e] Refractive index increment. [f] Arm numbers per molecule = (mole fraction of MMA) × M_w(star)/M_w(arm). [g] Mean radius of gyration by MALLS. [h] Calculated from the areas of SEC curves.

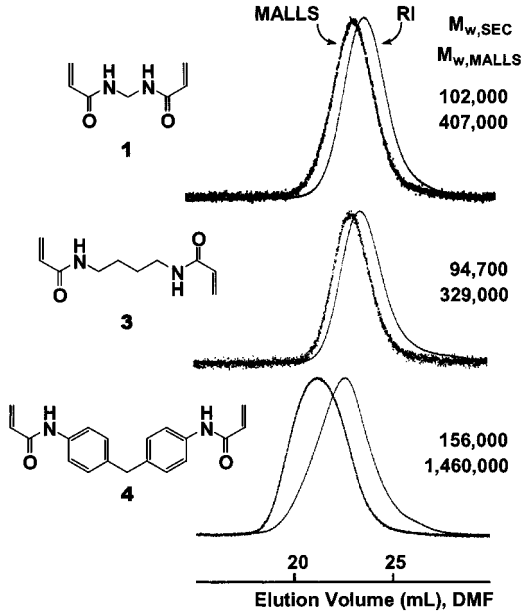


Figure 5. MALLS and SEC curves of the fractionated core-functionalized star polymers obtained from living poly(MMA) and **1**, **3**, and **4**. See Figure 3 for the reaction conditions.

microgel core, which might cause the difference in refractive index between the two moieties and thereby cause errors in MALLS/SEC analysis.[29] In the following part of this study, we therefore utilized **1**, an aliphatic linking agent that also gave star polymers in high yield as does **4**.

Core Sizes and Arm Lengths. Core-functionalized star polymers with various arm lengths and core sizes could be synthesized by changing the following two factors, among others:[16] the average degree of polymerization of arm chains (DP = $[MMA]_0/[P^*]_0 = [MMA]_0/[initiator]_0$) and the mole ratio of a linking agent to P* ($r = [\mathbf{1}]_0/[P^*]_0$); the latter determines the core size. Figure 6 summarizes nine experiments where the two factors were systematically varied.

First, the yield of star polymers was examined as the ratio r was changed while the arm length (DP) was kept constant. The products were obtained at 25 h after **1** had been added. The yield increased as r increased. For example, in the series B, E, and H for DP (arm) = 100, the yield increased from 75% (B) to 91% (H) as r was increased from 10 to 40. Note, however, that a too large r led to an insoluble gel (Figure 6G) due to a too high amount of the linking agent. The yield also increased as the degree of polymerization of arm chains (DP) increased while r kept unchanged. For example, in the series A−C with $r = 10$, the yield similarly increased from 64% (A; DP = 50) to 74% (C; DP = 200). Thus, appropriate design of the reaction condition was important for the synthesis of the star-shaped polymers with various core sizes and arm length in high yields.

Table 2 summarizes MALLS/SEC characterization results for the five samples given in Figure 6. The absolute molecular weight M_w ranged from 3.9×10^5 to 1.3×10^7, the arm numbers f from 20 to 640, and the gyration radii R_z from 5 to 42 nm. In the first three samples with the same arm DP, M_w clearly increased with increasing r, which in turn led to increasing arm number f (up to > 640) as well as increasing R_z. In particular, sample H is an extremely large star polymer of $M_w > 1.3 \times 10^7$ (MALLS), more than 640 arms per molecule, and R_z as large as >42 nm. The M_w values were almost unchanged by the sample concentrations and around $(1-2) \times 10^7$. This may exclude the possibility of aggregation of the star polymers under the measurement conditions. Such a high molecular weight might be ascribed to possible star−star coupling reaction while the SEC curves did not indicate that this is the main cause. A simple calculation from r and f shows that this polymer's core contains more than 5.1×10^4 ($= r \times f \times 2 = 40 \times 637 \times 2$) amide groups on average, which are confined into a microgel sphere with a radius smaller than 42 nm ($< R_z$). Though less impressive than this, other samples listed in Table 2 also carry large

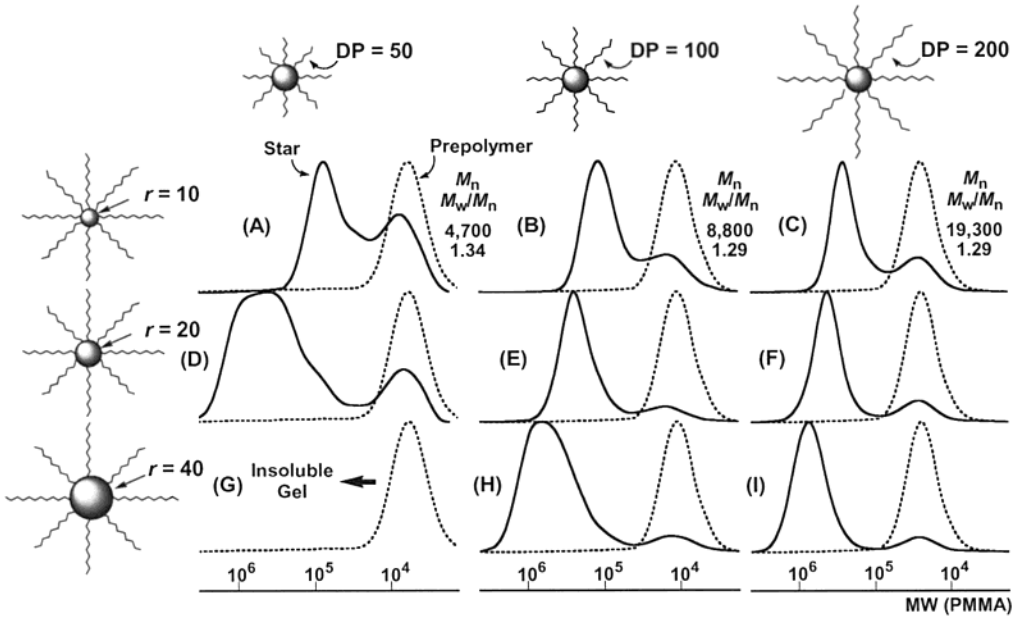


Figure 6. Star-shaped polymers with various functionalized core sizes and arm lengths obtained from living poly(MMA)s and **1** in toluene/DMF (5/3, v/v) at 80 °C: DP (arm) = $[MMA]_0/[P^*]_0$; $r = [\mathbf{1}]_0/[P^*]_0$; $[P^*]_0 = 20$ mM. Polymerization conditions: $[MMA]_0$ = 1.0 M−4.0 M; $[(MMA)_2-Cl]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[Al(O\text{-}i\text{-}Pr)_3]_0 = 40$ mM; $[\mathbf{1}]_0 = 200-400$ mM. (A−C): DP = 50−200; $r = 10$. (D−F): DP = 50−200; $r = 20$. (G−I): DP = 50−200; $r = 40$.

Table 2. Star-Shaped Polymers with Various Core Sizes and Arm Lengths[a]

sample in Figure 6	DP[b]	r[c]	M_w (arm) (SEC)[d]	M_w/M_n (arm) (SEC)	M_w (star) (SEC)	M_w (star) (MALLS)[e]	dn/dc[f] (mL/g)	f[g]	R_z[h] (nm)	yield[i] (%)
B	100	10	12 700	1.34	140 000	670 000	0.067	45	12.8	75
E	100	20	12 700	1.34	243 000	1 210 000	0.069	71	13.3	87
H	100	40	13 700	1.34	639 000	13 300 000	0.074	637	41.9	91
C	200	10	28 800	1.20	245 000	730 000	0.061	23	11.9	74
A	50	10	8 430	1.26	130 000	394 000	0.074	34	5.20	64

[a] Reaction conditions: MMA and divinyl compound **1** with $(MMA)_2-Cl/RuCl_2(PPh_3)_3/Al(Oi\text{-}Pr)_3$ in the mixture of toluene and DMF (5/3, v/v) at 80 °C. [b] Average degree of polymerization of arm chains (DP = $[MMA]_0/[P^*]_0 = [MMA]_0/[initiator]_0$). [c] Mole ratio of linking agent to P* ($r = [\mathbf{1}]_0/[P^*]_0$). [d] Size-exclusion chromatography. [e] Multiangle laser light scattering. [f] Refractive index increment. [g] Arm numbers per molecule. [h] Mean radius of gyration by MALLS. [i] Calculated from the areas of SEC curves.

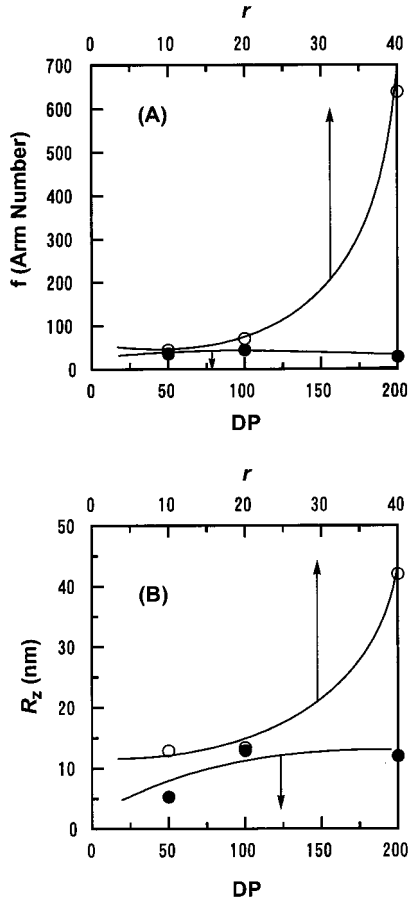


Figure 7. Arm number (f) and gyration radius (R_z) of core-functionalized star polymers as functions of DP (arm) and r (core).

numbers of core functions in relatively large star polymers.

The dependences of f and R_z on r and DP are visualized in Figure 7, which overall indicates that the ratio r (or the core size) is the primary factor that controls the star polymer formation.

Other Functionalized Microgel Cores. In addition to the bifunctional acrylamides (**1**−**4**), other divinyl compounds were examined as functionalized linking agents: an acrylamide (**5**) with two hydroxyl groups in the spacer, a methacrylamide (**6**) similar to **1**, and methacrylate (**7**) with a spacer hydroxyl group. Solutions of these compounds (**5** and **6**: in DMF, **7**: in toluene) were added into a well-defined living poly(MMA) to produce core-functionalized star polymers in 25 h. Figure 8 shows the results.

For example, amide **5** led to star polymers in a poor yield (Figure 8A), although it had a structure similar to **2** (Scheme 1), an acrylamide that gave star polymers efficiently (Figure 3B). The methacrylamide **6** and the methacrylate **7**, in contrast, gave high yields (>85%; Figure 8B,C). These results showed that the star polymers with various functionalized microgel cores (some with both amides and hydroxyls) could be synthesized by the design of linking agents.

Conclusions We have demonstrated that core-functionalized star poly(MMA)s can be synthesized in high yields by the linking reaction between living poly(MMA)s and various functionalized divinyl compounds in the Ru(II)-catalyzed living radical polymerization. Acrylamide-, methacrylamide-, and methacrylate-type functionalized divinyl compounds were suited for the synthesis, and thereby amide and alcoholic functions can be incorporated into microgel cores. Additionally, these star polymers have extremely large molecular weights, and perhaps more important, their cores carry a large number (up to 5.1×10^4) of polar functional groups that are confined at a high concentration into a presumably spherical microgel core. The characterization and functions of these cores in the star polymers will be the subjects of our forthcoming publication.

Experimental Section

Materials. Methyl methacrylate were of commercial source (Tokyo Kasei; purity >99%), dried overnight over calcium chloride, and purified by double distillation from calcium hydride before use. $(MMA)_2-Cl$ was prepared according to the literature.[26] Divinyl compounds (**1**: Tokyo Kasei, purity >98%; **5**: Aldrich, purity >97%; **6**: Tokyo Kasei) were purified recrystallization from methanol. Divinyl compound **2** (Aldrich) was used as received. Divinyl compound **7** (Aldrich, purity >85%, a mixture of isomers) was purified by passing through an inhibitor removal column (Aldrich; catalog no. 30, 631-2) before use.

Divinyl compound **3** was prepared with slight modification of a reported method:[30] In a 300 mL round-bottomed flask filled with dry nitrogen, a solution of acryloyl chloride (Tokyo Kasei, purity >95%; 26.3 mL, 0.326 mol) in acetonitrile (50 mL) was added dropwise to a solution of 1,4-diaminobutane (Tokyo Kasei, purity >98%; 13.1 g, 0.149 mol) in acetonitrile (50 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 30 min and then at 25 °C for an additional 4 h to give a white solid product. This product was filtered off, washed with acetonitrile (200 mL), and dried under vacuum. The white powder was then recrystallized from a mixture of methanol and water (7/3, v/v at −28 °C).

Divinyl compound **4** was prepared as follows: In a 500 mL round-bottomed flask filled with dry nitrogen, acryloyl chloride (Tokyo Kasei, purity >95%; 25.7 mL, 0.318 mol) was added dropwise to a solution of 4,4′-methylenedianiline (Aldrich, purity >97%; 25.3 g, 0.128 mol) and triethylamine (Tokyo Kasei >99%; 70.8 mL 0.511 mol) in ether (200 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 30 min and then at 25 °C for an additional 12 h to give a yellow solid product. This product was filtered off, washed with ether (300 mL), and dried under vacuum. The yellow powder was then recrystallized from methanol at −28 °C. ^{1}H NMR (500.16 MHz, DMF-

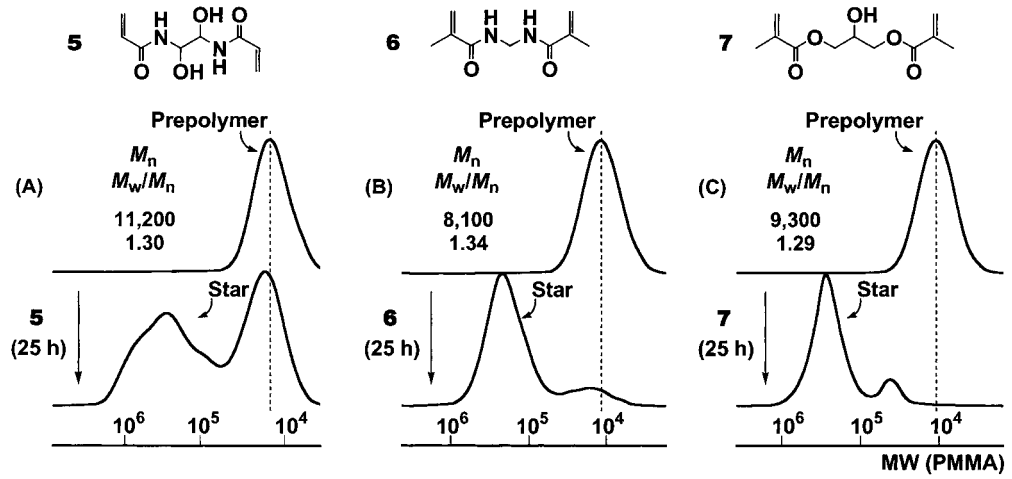


Figure 8. Core-functionalized star polymers obtained from living poly(MMA) with divinyl compounds **5**−**7** (see Scheme 1) in toluene/DMF (5/3, v/v for **5** and **6**) and in toluene (for **7**) at 80 °C: $[P^*]_0 = 20$ mM; DP (arm) = 100; $r = 20$.

d_7): δ 3.91 (s, 2H, CH_2), 5.72, 6.31 (d, 4H, CH_2, $J_{app} = 9.9$ and 16.8 Hz, respectively), 6.53 (dd, 2H, CH, $J_{app} = 10.1$, 17.0 Hz), 7.20 (d, 4H, CH, $J_{app} = 4.0$ Hz), 7.69 (d, 4H, CH, $J_{app} = 4.0$ Hz), 10.18 (s, 2H, NH).

$RuCl_2(PPh_3)_3$ (Merck, >99%) and Al(O*i*-Pr)$_3$ (Aldrich, >99.99%) were used as received. These compounds were handled in a glovebox under a moisture- and oxygen-free argon atmosphere (H_2O < 1 ppm, O_2 < 1 ppm). Toluene (solvent) and internal standards for gas chromatography (*n*-octane for MMA) were dried overnight over calcium chloride and distilled twice from calcium hydride. DMF (Wako, infinite pure; solvent for **1**−**6**) was used as received. The solvents bubbled with dry nitrogen for more than 15 min immediately before use.

Polymerization Procedures. The polymerization was carried out by the syringe technique under dry nitrogen in baked glass tubes equipped with a three-way stopcock. A typical procedure with $(MMA)_2$−Cl/$RuCl_2(PPh_3)_3$/Al(O*i*-Pr)$_3$/**1** follows: The polymerization was initiated by adding MMA (0.428 mL), *n*-octane (0.075 mL), a solution of $(MMA)_2$−Cl (0.048 mL, 832 mM in toluene), and Al(O*i*-Pr)$_3$ (0.64 mL, 125 mM in toluene) in toluene, sequentially in this order, into $RuCl_2(PPh_3)_3$ (0.8 mL, 25 mM in toluene) in toluene at 25 °C. Immediately after mixing, the mixture was placed in an oil bath kept at 80 °C. After the polymerization had reached over ca. 88% conversion in 94 h, a solution of **1** (1.0 mL, 0.8 M in DMF) was added to the unquenched solution. The reaction was terminated by cooling the mixture to −78 °C. The conversion of the MMA was determined from the concentrations of the residuals measured by gas chromatography with the internal standards as *n*-octane. The conversion of **1** was determined from the ratio of the peak areas of the olefin groups derived from **1** to those of DMF by ^{1}H NMR spectra (**1** was consumed ca. 100% after 25 h). The quenched reaction mixtures were diluted with toluene (ca. 20 mL) and rigorously shaken with an absorbent [Kyowaad-2000G-7 ($Mg_{0.7}Al_{0.3}O_{1.15}$); Kyowa Chemical] (ca. 5 g) to remove the metal-containing residues. After the absorbent was separated by filtration (Whatman 113V), the filtrate was evaporated to dryness to give the products, which were subsequently dried overnight under vacuum at room temperature. For example, the yield of the products obtained at 25 h after addition of **1** under the condition for Figure 3 was 54% due to partial loss of polymers by the absorbent. The M_n and M_w/M_n values for the higher molecular weight fraction of the products were 1.02×10^5 and 1.40, respectively (**1** in Table 1).

Polymer Characterization. The MWD, M_n, and M_w/M_n ratios of the polymers were measured by SEC in DMF containing 10 mM LiBr at 40 °C (flow rate: 1 mL/min) on three linear-type polystyrene gel columns (Shodex KF-805L; exclusion limit = 5×10^6; pore size = 20−1000 Å; 0.8 cm i.d. × 30 cm) that were connected to a Jasco PU-980 precision pump, a Jasco RI-930 refractive index detector, and a Jasco UV-970 UV/vis detector set at 256 nm. The columns were calibrated against 13 standard poly(MMA) samples (Polymer Laboratories; M_n = 200−1 200 000; M_w/M_n = 1.06−1.22) as well as MMA monomer. ^{1}H NMR spectra were recorded in $CDCl_3$ at 25 °C on a JEOL JNM-LA500 spectrometer, operating at 500.16 MHz. Polymer samples for ^{1}H NMR and MALLS analysis were fractionated by preparative SEC (column: Shodex K-5003). The weight-average molecular weight (M_w) of the polymers was determined by multiangle laser light scattering (MALLS) in DMF containing 10 mM LiBr at 40 °C on a Dawn E instrument (Wyatt Technology; Ga−As laser, λ = 690 nm). The refractive index increment (d*n*/d*c*) was measured in DMF at 40 °C on a Photal DRM-1020 refractmeter (Otsuka Electronics; λ = 690 nm, c < 8.0 mg/mL). Some values are found in Tables 1 and 2. Infrared spectra were recorded on a Perkin Elmer System 2000 FT-IR.

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References and Notes

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(2) For reviews, see: (a) Bauer, B. J.; Fetters, L. J. *Rubber Chem. Technol.* **1978**, *51*, 406. (b) Bywater, S. *Adv. Polym. Sci.* **1979**, *30*, 90. (c) Marsalkó, T. M.; Majoros, I.; Kennedy, J. P. *Pure Appl. Chem.* **1997**, *A34*, 775.

(3) For reviews on synthesis of star-shaped polymers by ionic living polymerizations, see: (a) Morton, M. *Anionic Polymerization*: *Principle and Practice*; Academic Press: New York, 1983; pp 221−232. (b) Hsieh, H. L.; Quirk, R. P. *Anionic Polymerization*; Marcel Dekker: New York, 1996; pp 333−368. (c) Simms, J. A.; Spinelli, H. J. In *Macromolecular Design of Polymeric Materials*; Hatada, K., Kitayama, T., Vogl, O., Eds.; Marcel Dekker: New York, 1997; pp 379−391. (d) Sawamoto, M. In *Cationic Polymerization*; Matyjaszewski, K., Ed.; Marcel Dekker: New York, 1996; pp 412−420. (e) Sawamoto, M.; Kamigaito, M. In *New Methods of Polymer Synthesis*; Ebdon, J. R., Eastmond, G. C., Eds.; Blackie: Glasgow, 1995; Vol. 2, pp 37−68. (f) Sawamoto, M.; Kanaoka, S.; Higashimura, T. In *Hyper-Structured Molecules I: Chemistry, Physics and Applications*; Sasabe, H., Ed.; Gordon and Breach Science Publishers: Amsterdam, 1999; pp 43−61.

(4) Hawker, C. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1456.

(5) Solomon, D. H. *Macromol. Rapid Commun.* **1997**, *18*, 755.

(6) Ueda, J.; Matsuyama, M.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1998**, *31*, 557.
(7) Ueda, J.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1998**, *31*, 6762.
(8) Angot, S.; Murthy, K. S.; Taton, D.; Gnanou, Y. *Macromolecules* **1998**, *31*, 7218.
(9) Matyjaszewski, K.; Miller, P. J.; Pyun, J.; Kickelbick, G.; Diamanti, S. *Macromolecules* **1999**, *32*, 6526.
(10) Haddleton, D. M.; Edmonds, R.; Heming, A. M.; Kelly, E. J.; Kukulj, D. *New J. Chem.* **1999**, *23*, 477.
(11) Angot, S.; Murthy, K. S.; Taton, D.; Gnanou, Y. *Macromolecules* **2000**, *33*, 7261.
(12) Heise, A.; Nguyen, C.; Malek, R.; Hendrick, J. L.; Frank, C. W.; Miller, R. D. *Macromolecules* **2000**, *33*, 2346.
(13) McAlvin, J. E.; Scott, S. B.; Fraser, C. L. *Macromolecules* **2000**, *33*, 6953.
(14) Xia, J.; Zhang, X.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 4482.
(15) Zhang, X.; Xia, J.; Matyjaszewski, K. *Macromolecules* **2000**, *33*, 2340.
(16) Baek, K.-Y.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2001**, *34*, 215.
(17) Chong, Y. K.; Le, T. P. T.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1999**, *32*, 2071.
(18) Hedrick, J. L.; Trollsås, M.; Hawker, C. J.; Atthoff, B.; Claesson, H.; Heise, A.; Miller, R. D.; Mecerreyes, D.; Jérome, R.; Dubois, Ph. *Macromolecules* **1998**, *31*, 8691.
(19) Angot, S.; Taton, D.; Gnanou, Y. *Macromolecules* **2000**, *33*, 5418.
(20) Yijin, X.; Caiyuan, P. *Macromolecules* **2000**, *33*, 4750.
(21) For recent reviews on living radical polymerization, see: (a) Georges, M. K.; Vergin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Trends Polym. Sci.* **1994**, *2*, 66. (b) Davis, T. P.; Kukulj, D.; Haddleton, D. M.; Maloney, D. R. *Trends Polym. Sci.* **1995**, *3*, 356. (c) Hawker, C. J. *Trends Polym. Sci.* **1996**, *4*, 183. (d) Sawamoto, M.; Kamigaito, M. *Trends Polym. Sci.* **1996**, *4*, 371. (e) Colombani, D. *Prog. Polym. Sci.* **1997**, *22*, 1649. (f) Hawker, C. J. *Acc. Chem. Res.* **1997**, *30*, 373. (g) Sawamoto, M.; Kamigaito, M. *Polymer Synthesis* (*Materials Science and Technology Series*); Schülter, A.-D., Ed.; VCH-Willey: Weinheim, Germany, 1999; Chapter 6. (h) Sawamoto, M.; Kamigaito, M. *CHEMTECH* **1999**, *29* (6), 30. (i) Matyjaszewski, K. *Acc. Chem. Res.* **1999**, *32*, 895.
(22) (a) Zilliox, J. G.; Rempp, P.; Parrod, J. *J. Polym. Sci., Part C* **1968**, *22*, 145. (b) Worsfold, D. J.; Zilliox, J. G.; Rempp, P. *Can. J. Chem.* **1969**, *47*, 3379.
(23) Kanaoka, S.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1993**, *26*, 254.
(24) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721.
(25) Ando, T.; Kato, M.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1996**, *29*, 1070.
(26) Ando, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1998**, *31*, 6708.
(27) Ando, T.; Kamigaito, M.; Sawamoto, M. *Tetrahedron* **1997**, *53*, 15445.
(28) Ando, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2000**, *33*, 2819.
(29) Kanaoka, S.; Hayase, N.; Higashimura, T. *Polym. Bull.* **2000**, *44*, 485.
(30) Lee, S. K.; Seo, K. H.; Kim, W. S. *Polymer* **1993**, *34*, 2392.

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